HIGH-CAPACITY HYDROGEN STORAGE ALLOY AND

METHOD FOR PRODUCING THE SAME

BACKGROUND OF THE INVENTION

The present invention relates to a hydrogen storage alloy used as a material for hydrogen storage, a hydrogen absorbing material for thermal conversion, a hydrogen supply material for fuel battery, a negative electrode material for nickel-hydrogen battery, a material for hydrogen purification and recovery, a hydrogen absorbing material for hydrogen gas actuator, or the like, and particularly relates to a high-capacity hydrogen storage alloy having excellent property at a temperature near the room temperature, and a method for producing the high-capacity hydrogen storage alloy.

Although a gas cylinder system and a liquid hydrogen system have been heretofore used for storage and transportation of hydrogen, a system using a hydrogen storage alloy has begun to be noticed as an alternative to these systems. As well known, a hydrogen storage alloy has a property of reversibly reacting with hydrogen to absorb/release the hydrogen with incoming/outgoing of reaction heat. This chemical reaction is used for attaining practical application of a technique for storage and transportation of hydrogen. Moreover, the reaction heat is used for promoting development and practical application of a technique for constructing a

1

heat storage and heat transportation system or the like. $LaNi_5$, TiFe, $TiMn_{1.5}$, or the like, is known well as a representative hydrogen storage alloy.

For practical application of the hydrogen storage alloy to various kinds of purposes, it is necessary to improve the property of the hydrogen absorbing material more greatly. For example, increase in hydrogen capacity, reduction in cost of raw materials, improvement in plateau property, improvement in durability, etc are the important issues. Especially, it has been known from long time ago that metal of a body-centered cubic structure (hereinafter referred to as "BCC") such as V, a TiVMn type alloy or a TiVCr type alloy can absorb a great quantity of hydrogen compared with an AB_5 type or AB_2 type alloy which has been already put into practical use.

V, a TiVMn type alloy, a TiVCr type alloy, or the like, capable of absorbing a large quantity of hydrogen, however, lacks practical applicability because expensive V must be used so that a hydrogen storage material using V increases raw material cost.

Although it is known that V or a TiVMn type or TiVCr type alloy can absorb about 400 cc/g of hydrogen, there is also a disadvantage that efficiency of the V or TiVMn type or TiVCr type alloy is poor because the quantity of hydrogen allowed to be absorbed/released effectively is about a half of the

2

aforementioned quantity so that the residual part of the alloy is chemically combined with hydrogen and remains as a solid-soluble phase. In addition, there are various difficulties to put the alloy into practical use because the percentage of deterioration of the alloy increases as absorption/release of hydrogen is repeated and because equilibrium dissociation pressure decreases rapidly as the number of hydrogen absorption/release cycles increases.

SUMMARY OF THE INVENTION

Basically, the present invention is to solve the aforementioned problems and an object thereof is to provide a hydrogen storage alloy which can absorb/release hydrogen effectively at normal temperature without containing V and which exhibits an excellent capacity of hydrogen absorption and an rechargeable hydrogen capacity compared with a conventional material and exhibits excellent durability.

To solve the aforementioned problems, according to a first aspect of the prevent invention, there is provided a high-capacity hydrogen storage alloy comprising a crystal structure containing a body-centered cubic structure as a single or main phase and made of a composition represented by the general formula $Ti_aCr_bMo_c$
in which $\underline{a}$ is in a range of from 25 to 45 % by atomic weight,

3

$\underline{b}$ is in a range of from 30 to 65 % by atomic weight, and $\underline{c}$ is

in a range of from 5 to 40 % by atomic weight.

According to a second aspect of the present invention,

there is provided a high-capacity hydrogen storage alloy

comprising a crystal structure containing a body-centered

cubic structure as a single or main phase and made of a

composition represented by the general formula $Ti_aCr_bMo_cFe_d$.

in which $\underline{a}$ is in a range of from 25 to 45 % by atomic weight,

$\underline{b}$ is in a range of from 30 to 65 % by atomic weight, $\underline{c}$ is in

a range of from 5 to 40 % by atomic weight, and $\underline{d}$ is not larger

than 15 % by atomic weight.

According to a third aspect of the present invention,

there is provided a method for producing a high-capacity

hydrogen storage alloy, comprising the steps of: applying a

heat treatment to a material made of a composition defined in

Claim 1 or 2 to thereby heat the material at a temperature in

a range of from 1,200 to 1,500°C for 1 minute to 24 hours; and

cooling the material at a cooling speed equal to or higher than

the speed of water cooling after the heat treatment.

BRIEF DESCRIPTION OF THE DRAWINGS

Fig. 1 is a hydrogen pressure-composition isothermal

curve (PCT curve) graph of a material obtained by applying a

water-cooling treatment to an alloy (material according to the

present invention) having a composition $Ti_{36}Cr_{53}Mo_{11}$ (atomic ratio: $TiCr_{1.5}Mo_{0.3}$) after a heat treatment at $1,450°C$ for 1 minute;

Fig. 2 is a PCT curve graph of a material obtained by applying a water-cooling treatment to an alloy (material according to the present invention) having a composition $Ti_{36}Cr_{53}Mo_{11}$ (atomic ratio: $TiCr_{1.5}Mo_{0.3}$) after a heat treatment at $1,450°C$ for 1 minute or at $1,300°C$ for 3 hours;

Fig. 3 is a PCT curve graph of a material obtained by applying a water-cooling treatment to an alloy (material according to the present invention) having a composition $Ti_{36}Cr_{57}Mo_{7}$ (atomic ratio: $TiCr_{1.6}Mo_{0.2}$) after a heat treatment at $1,300°C$ for 3 hours;

Fig. 4 is a PCT curve graph of an alloy (conventional material) of $Ti_{36}Cr_{53}V_{11}$ (atomic ratio: $TiCr_{1.5}V_{0.3}$) after repetition of hydrogen absorption/release;

Fig. 5 is a PCT curve graph of an alloy (material according to the present invention) of $Ti_{36}Cr_{53}Mo_{11}$ (atomic ratio: $TiCr_{1.5}Mo_{0.3}$) after repetition of hydrogen absorption/release;

Fig. 6 is a PCT curve graph of an alloy of $Ti_{36}Cr_{53}Mo_{9}V_{2}$ (atomic ratio: $TiCr_{1.5}Mo_{0.25}V_{0.05}$) after repetition of hydrogen absorption/release;

Fig. 7 is a PCT curve graph of an alloy of $Ti_{36}Cr_{53}Mo_{2}V_{9}$ (atomic ratio: $TiCr_{1.5}Mo_{0.05}V_{0.25}$) after repetition of hydrogen

absorption/release;

Fig. 8 shows a result of X-ray diffraction measurement of an alloy of $Ti_{36}Cr_{53}Mo_{11-x}V_x$ (atomic ratio: $TiCr_{1.5}Mo_{0.3-x}V_x$) after repetition of hydrogen absorption/release;

Fig. 9 shows a result of X-ray diffraction measurement of an alloy (material according to the present invention) of $Ti_{36}Cr_{53}Mo_{11}$ (atomic ratio: $TiCr_{1.5}Mo_{0.3}$);

Fig. 10 is a PCT curve graph of an alloy (material according to the present invention) of $Ti_{36}Cr_{57}Mo_7$ (atomic ratio: $TiCr_{1.6}Mo_{0.2}$) containing a large quantity (3,250 ppm) of oxygen;

Fig. 11 is a PCT curve graph of an alloy (material according to the present invention) of $Ti_{36}Cr_{57}Mo_7$ (atomic ratio: $TiCr_{1.6}Mo_{0.2}$) containing a small quantity (980 ppm) of oxygen.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENT

The reason why the composition and producing condition are determined in the present invention will be described below.

As described above, the present invention provides a crystal structure containing a body-centered cubic structure (hereinafter properly referred to as "BCC") as a single or main phase and made of a ternary alloy containing Ti, Cr and Mo as constituent elements, or a quarternary alloy further containing Fe as an additive element in addition to Ti, Cr and Mo. If another crystal structure is used, good plateau

property cannot be obtained.

Here, the component percentage of Ti is selected to be in a range of from 25 to 45 % by atomic weight (hereinafter properly referred to as "at%"). If the component percentage of Ti is smaller than 25 at%, the resulting alloy can be hardly initially activated and the hydrogen absorption capacity of the alloy is lowered to thereby make the practical use of the alloy impossible. If the component percentage of Ti is larger than 45 at%, the plateau property is worsened. Accordingly, the component percentage of Ti is selected to be in the aforementioned range. For the same reason as described above, it is preferable that the lower limit and the upper limit are 30 at% and 40 at% respectively.

Next, the component percentage of Cr is selected to be in a range of from 30 to 65 at%. If the component percentage of Cr is smaller than 30 at%, plateau property is worsened. On the other hand, if the component percentage of Cr is larger than 65 at%, the capacity of each of the hydrogen absorption and release is lowered. Accordingly, the component percentage of Cr is selected to be in the aforementioned range. For the same reason as described above, it is further preferable that the lower limit and the upper limit are 47 at% and 57 at% respectively.

Mo is added as an element substituted for a part of Cr.

7

The tendency of the change of PCT property after repetition of hydrogen absorption/release varies widely in accordance with the quantity of Mo substituted for a part of Cr. As shown in Fig. 4, in an alloy (conventional material: $Ti_{36at\%}Cr_{53at\%}V_{11at\%}$) obtained by adding V to a Ti-Cr binary alloy, absorption/release pressure decreases largely in accordance with the repetition of absorption/release (see Fig. 4). In an alloy (material according to the present invention: $Ti_{36at\%}Cr_{53at\%}Mo_{11at\%}$) obtained by adding only Mo to the Ti-Cr binary alloy, however, reduction in pressure is small (see Fig. 5). When the Mo and V contents of a TiCrMoV quarternary alloy are changed as a reference example, it is understood that the change of pressure decreases as the quantity of addition of Mo increases (see Figs. 6 and 7). Particularly when the quantity of addition of Mo is large, the change of release pressure accompanying the repetition of hydrogen absorption/release is so small that the alloy becomes very easy to be handled when it is applied to a system. When the structural change of the alloy is measured by X-ray diffraction after hydrogen absorption/release is repeated by 500 times, it is found that the X-ray diffraction peak becomes higher as the quantity of addition of Mo increases (see Fig. 8). This means that, as the quantity of Mo in the composition increases, the crystallinity of the alloy is kept high even after repetition of hydrogen absorption/release. That is, it is found that the

8

material according to the present invention exhibits good property also in durability against repetition of hydrogen absorption/release because the BCC structure is stabilized by addition of Mo.

Taking durability against repetition of hydrogen absorption/release into account, the TiCrMo type alloy, which is a material obtained by addition of Mo according to the present invention, is an alloy small in the change of equilibrium dissociation pressure owing to repetition of hydrogen absorption/release and very easy to be handled in comparison with a TiCrV type alloy used in the related art. However, if the quantity of addition of Mo is larger than 40 at%, the maximum hydrogen absorption capacity decreases remarkably. On the other hand, if the quantity of addition of Mo is smaller than 5 at%, the BCC structure of the alloy is hardly stabilized. Accordingly, the quantity of Mo is selected to be in a range of from 5 to 40 at%. For the same reason as described above, it is further preferable that the lower limit and the upper limit are 7 at% and 10 at% respectively.

Further, in order to adjust the equilibrium dissociation pressure, Fe may be added as occasion demands. However, if the quantity of addition of Fe is larger than 15 at%, the BCC

structure of the alloy is not stabilized. Accordingly, the quantity of Fe is selected to be not larger than 15 at%. For the same reason as described above, it is further preferable that the upper limit is 7 at%.

The adjustment of the equilibrium dissociation pressure may be performed by changing the Ti/Cr ratio in the composition.

It has been also already found that hydrogenation property is worsened remarkably when the oxygen content of a TiCrV type BCC alloy is large. When the oxygen content increases, the influence of increase in equilibrium dissociation pressure, great reduction in hydrogen absorption capacity, deterioration in plateau property, etc. is observed remarkably. In a TiCrMo type BCC alloy, however, a large and flat plateau portion is exhibited even though the oxygen content is relatively large. Figs. 10 and 11 show the difference in hydrogenation property between a TiCrMo alloy containing a large quantity of oxygen and a TiCrMo alloy containing a small quantity of oxygen for reference. As shown in Figs. 10 and 11, equilibrium dissociation pressure varies and the plateau width thereof varies slightly in accordance with the oxygen content. In each of Figs. 10 and 11, however, a relatively large plateau portion is obtained. That is, it would be said that the TiCrMo alloy is not affected by oxygen compared with the TiCrV alloy.

10

As described above, also in a TiCrMo alloy or a TiCrMoFe alloy, property of a flat and large plateau portion is obtained similarly to that in the TiCrV alloy if the TiCrMo or TiCrMoFe alloy has a predetermined composition and contains a BCC structure as a single or main phase (see Fig. 1). It is, however, preferable that a heat treatment for production of the alloy is performed at a temperature in a range of from 1,200 to 1,500°C and that the cooling speed after the heat treatment is equal to or higher than the speed obtained by water cooling. It has been already confirmed that a solution treatment can be made sufficiently to obtain good hydrogenation property if the heat treating time is not shorter than 1 minute upon production of the alloy (see Fig. 1). In comparison between an alloy heat-treated at 1,300°C for 3 hours and an alloy heat-treated at 1,450°C for 1 minute according to the present invention, each alloy exhibits substantially equal property. Accordingly, it is found that excellent hydrogenation property can be exhibited even in the case where the heat treatment is carried out for about 1 minute (see Fig. 2). In accordance with compositions, however, the BCC structure may be unable to be obtained in the heat treatment at about 1,200°C, so that hydrogenation property may be worsened. In a composition shown in Fig. 3, different phases are precipitated even in the heat treatment at 1300°C, so that property is worsened. It

11

is, therefore, necessary to perform the heat treatment suitably in the heat treatment range described in the Scope of Claim for a patent, in accordance with the composition.

It is found from the above results that a BCC single phase is exhibited by each of almost all the compositions in the heat treatment condition in which the heat-treating temperature is in the range defined according to the present invention, that is, in a range of from 1,200 to 1,500°C, and that the BCC single phase can be obtained sufficiently even in the case where the heat-treating time is about 1 minute. To obtain better property, it is preferable that a solution treatment is carried out at a temperature as high as possible but within the range not to melt the alloy in the heat treatment. Further, the alloy can be made sufficiently soluble even in the case where the heat-treating time is selected to be as short as possible in accordance with the ingot size of the alloy. To obtain the BCC single phase structure, it is preferable that a cooling method using a cooling speed as high as possible is used after the heat treatment. However, even in the case where the BCC single phase cannot be obtained perfectly, there is no large deterioration of property. Fig. 9 shows a result of X-ray diffraction measurement of $Ti_{35.7at\%}Cr_{53.6at\%}Mo_{10.7at\%}$ (which is equivalent to $TiCr_{1.5}Mo_{0.3}$ in quantitative ratio and which is the same alloy composition as shown in Fig. 1). In Fig. 9,

12

different phase peaks are observed in respective neighbors of 37°, 62° and 75° but hydrogenation property is good as shown in Fig. 1.

As described above, a cooling method in which a cooling speed as high as possible is obtained is preferably used for cooling after the heat treatment. Therefore, a cooling speed equal to or higher than the cooling speed obtained by water cooling is used. An example of the cooling method includes quenching or roll quenching using gas cooling or water cooling.

That is, in accordance with the present invention, hydrogen can be absorbed/released effectively in various temperature ranges by the operation of components Ti, Cr, Mo and Fe, and plateau property is good. In addition, the alloy exhibits excellent durability against hydrogen absorption/release and exhibits excellent property particularly against the change of equilibrium dissociation pressure. Accordingly, hydrogen storage/transportation efficiency can be improved, so that the quantity of effective hydrogen migration can be kept excellent even in the case where the alloy is used for a long term.

(Examples)

Examples according to the present invention will be described below in comparison with Comparative Examples.

13

Component materials Ti, Cr and Mo (Fe) were weighed and mixed to achieve a target alloy. The mixture was received in a crucible of a vacuum arc dissolving apparatus and arc-dissolved under an atmosphere of high-purity Ar gas. Then, the mixture was cooled to room temperature in the apparatus and solidified. The alloy obtained thus was pulverized into a mesh size of from 50 to 200 in atmospheric air to thereby obtain samples to be measured. In a stainless steel reactor in a pressure-composition isothermal curve measuring apparatus, 5 g of each sample was enclosed.

A heat treatment was applied to the measurement sample in the condition of a temperature range of from 1,200 to 1,500°C for 1 minute to 24 hours. Then, the sample was cooled with water.

An activating treatment was performed as a pre-treatment before hydrogen absorption/release property of the sample was measured. That is, the reactor was heated at 80°C for about 1 hour while decompressed (to about 10^{-5} kgf/cm^2) and evaluated so that the reactor was degassed. Then, high-purity hydrogen with pressure of 50 kgf/cm^2 at 80°C was imported into the reactor. Then, the reactor was cooled to 20°C. By the aforementioned process, the sample began to absorb hydrogen immediately. After 30 minutes, the absorption of hydrogen was completed. The reactor was further evacuated while heated to 80°C to thereby desorb hydrogen from the sample. After these

14

processes were repeated by a plurality of times, the activating treatment was terminated.

Then, the hydrogen absorption/release property of each sample was measured. That is, after the reactor temperature was dropped to 20°C and kept at 20°C, a predetermined quantity of high-purity hydrogen was imported into the reactor. After hydrogen was absorbed to the sample and the pressure in the reactor was stabilized, the hydrogen pressure in the reactor was measured, and the quantity of hydrogen absorbed to the sample was measured by a constant-volume method. After a predetermined quantity of hydrogen was imported into the reactor again and the pressure was stabilized, the hydrogen pressure and the hydrogen absorption capacity were obtained. The aforementioned operation was repeated until the pressure in the reactor reached 50 kgf/cm^2. Thus, hydrogen pressure-absorption capacity-isothermal curves were obtained.

After hydrogen was absorbed to each sample until the pressure reached 50 kgf/cm^2 as described above, a predetermined quantity of hydrogen was discharged from the reactor while the reactor was kept at the aforementioned temperature of 20°C. After the hydrogen pressure in the reactor was stabilized, the pressure in the reactor and the quantity of hydrogen desorbed from the sample were measured by a constant-volume method. A

predetermined quantity of hydrogen was discharged from the reactor again. The aforementioned operation was repeated until the pressure in the reactor reached 0.2 kgf/cm^2. Thus, hydrogen pressure-release capacity-isothermal curves were obtained in a hydrogen release process (Figs. 1 to 3).

Such hydrogen pressure-composition isothermal curves (PCT curves) were plotted at various temperatures and the change of equilibrium dissociation pressure in each PCT curve was plotted with respect to 1/T (T represents the temperature expressed in K) to thereby calculate heat ΔH (kJ/molH$_2$) of reaction of the alloy. Results of the calculation were shown in Table 1.

Then, durability of each sample against repetition of hydrogen absorption/release was measured. In a stainless steel reactor in a durability evaluation testing apparatus, 2 g of each sample was enclosed. The same activating treatment as described above was applied and the reactor temperature was dropped to 20°C. Then, the same processes as in the aforementioned hydrogen absorption/release property measuring method were repeated. Thus, the change of the hydrogen absorption capacity in accordance with the number of repetition times was obtained by comparison between PCT curves (Figs. 4 to 7).

The reaction heat of the alloy sample in each of Example

16

according to the present invention exhibited a smaller value
than the reaction heat of the alloy sample in each of
Comparative Examples. Hence, it is preferable that the alloy
according to the present invention is used as a hydrogen supply
material not for heat pump but for fuel battery. As an example,
the maximum capacity of hydrogen absorption and the quantity
of effective hydrogen migration in $TiCr_{1.5}V_{0.3}$ (comparative
material) and those in $TiCr_{1.5}MO_{0.3}$ (material according to the
present invention) are shown in Table 2. As shown in Table
2, the ratio of the quantity of effective hydrogen migration
to the maximum capacity of hydrogen absorption in the material
according to the present invention is large compared with that
in the comparative material. That is, the material according
to the present invention can utilize a great deal of hydrogen
absorbing power in the alloy. Moreover, because the material
according to the present invention is small in the maximum
capacity of hydrogen absorption, it would be said that the
material according to the present invention is a low-expansion
alloy compared with the conventional material. This brings
increase in the percentage of alloy charged in a hydrogen
storage alloy tank and improvement in the handling property
of the tank. Accordingly, higher hydrogen storage density can
be achieved by use of the material according to the present
invention.

Table 1: Alloy Reaction Heat ΔH $(kJ/molH_2)$

Sample No.		Alloy Composition	Alloy Reaction Heat $|\Delta H|$ $(kJ/molH_2)$
Comparative Material	1	$TiCr_{1.5}V_{0.3}$	41.1081
	2	$TiCr_{1.4}V_{0.4}$	41.7538
Material according to the Invention	3	$TiCr_{1.5}Mo_{0.3}$	25.2636
	4	$TiCr_{1.4}Mo_{0.4}$	24.8324

Table 2: Maximum Hydrogen Capacity and Rechargeable Hydrogen Capacity

Sample		Maximum Hydrogen Capacity (cc/g)	Rechargeable Hydrogen Capacity (cc/g)
Comparative Material	$TiCr_{1.5}V_{0.3}$	391	220
Material according to the Invention	$TiCr_{1.5}Mo_{0.3}$	288	200

As described above, in the hydrogen storage alloy according to the present invention, hydrogen can be absorbed/released effectively in various temperature ranges by the operation of components Ti, Cr, Mo and Fe in the alloy, and plateau property is good. In addition, the alloy exhibits excellent durability against hydrogen absorption/release and exhibits excellent property particularly against the change of equilibrium dissociation pressure. Accordingly, hydrogen storage/transportation efficiency can be improved and the quantity of effective hydrogen migration can be kept excellent even in the case where the alloy is used for a long term.

18

As described above, the material according to the present invention is inexpensive compared with the TiCrV type alloy which is a material used in the related art, because V is not used in the material according to the present invention. Moreover, the material according to the present invention exhibits good hydrogenation property which is equivalent to that of the TiCrV type alloy, and there is little change of equilibrium dissociation pressure owing to repetition of hydrogen absorption/release. That is, the material according to the present invention is an alloy which is low in expansion and low in alloy reaction heat and which has such good property that the alloy can be handled easily.